5/8/03 #12

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Takao ABE et al. Group Art Unit: 1765

Application No.: 09/743,982 Examiner: M.A. Anderson

Filed: January 18, 2001 Docket No.: 108360

For: SILICON SINGLE CRYSTAL AND WAFER DOPED WITH GALLIUM AND METHOD FOR PRODUCING THEM

DECLARATION UNDER 37 C.F.R. §1.132

Director of the U.S. Patent and Trademark Office
Washington, D.C. 20231

Sir:

I, Takao Abe, a citizen of Japan, hereby declare and state:

1. I have a doctoral degree in Engineering, conferred upon me by the Faculty of Engineering of Hokkaido University in Japan in 1985.

2. I have been employed by Shin-Etsu Handotai Co., Ltd. since 1964 and I have had a total of 40 years of work and research experience in dislocated and dislocation-free silicon single crystals. The growing mechanism of intrinsic point defects and the suppression of point defects by doping nitrogen are particular subjects of my research. For these results, the Japan Association of Crystal Growth gave me the Paper Award in 1991. The demonstration of gallium-doped CZ crystals for solar cell application is one of these results. I have also performed research in the field of silicon-on-insulator structures created by wafer bonding techniques. These silicon-on-insulator structures are used for advanced ULSI devices. In addition, for mass production, I have contributed to developments

regarding the growth of dislocation-free FZ and CZ crystals, as opposed to dislocated crystals, and larger diameter FZ and CZ crystals from 10 mm FZ to 300 mm CZ crystals. Regarding other wafering processes, I developed, 15 years ago, new surface grinders to create flatter surfaces for bonded silicon-on-insulator wafers. These surface grinders are now popular in wafer technology. I was also involved in the development of many evaluation and characterization processes and equipment. The Solid State Materials and Devices (SSMD) Award was given by the Japanese Society of Applied Physics for the evaluation work by the technique of photoluminescence in cooperation with the public institution in 1992.

3. I am a member of the Electrochemical Society, the Japanese Society of Applied Physics and the Japanese Society of Physics. I was a co-organizer and co-chairman of the Silicon Materials Symposium and the Semiconductor Wafer Bonding Symposium from 1977 until 2002 in the Electrochemical Society Meetings held in the United States.

4. I have published numerous papers in this field, and applied for patents in the United States, Japan and other countries. In total, I have published more than 30 research papers in Japanese and more than 60 in English. A representative list of my English language publications related to silicon-on-insulator technology is attached hereto as Exhibit A.

5. I have applied for over 80 patents in Japan, and over 40 in the United States, of which 10 have been issued, and I have filed more than 200 other foreign applications.

6. In September of 1999, I participated in a conference, the 11th International Photovoltic Science and Engineering Conference ("PVSEC-11"), and published the paper presented there in the Technical Digest of the International PVSEC-11. This paper, Saitoh et al., *Light Degradation and Control of Low-Resistivity CZ-Si Solar Cells*, Technical Digest

of the International PVSEC-11, Sapporo, Hokkaido, Japan, 1999, presented my findings, the subject matter of the claims of the above-captioned patent application, that a gallium-doped silicon single crystal wafer can overcome the problem of photo-degradation occurring on a boron-doped wafer, and these wafers can be made into solar cells having a large area and high conversion efficiencies. This paper received a special award for excellence at PVSEC-11, given to the best research paper presented at the Conference. In addition, a number of researchers, representing various research institutes and listed on the paper, confirmed the results, which are internationally recognized.

7. After PVSEC-11, two papers were published by researchers at the Fraunhofer-Institute for Solar Energy Systems in Germany. I had asked these researchers to evaluate my findings, and these papers summarize the evaluation of my research as it relates to the conversion efficiencies and areas of gallium-doped silicon single crystal wafers. Conversion efficiencies of 22.5% and 20.2% for 2 x 2 cm^2 and 10 x 10 cm^2 gallium-doped silicon wafers respectively were reported in those papers. The results were surprising because it was known that the efficiency generally decreases as the area of a wafer increases. A conversion efficiency of 20% or more can not be achieved for a boron-doped silicon single crystal wafer having an area of 10 x 10 cm^2. The papers report the surprising result that a conversion efficiency of 20% or more was, for the first time, achieved for a gallium-doped silicon single crystal wafer with a large area.

8. I found, for the first time, that for solar cells made from gallium-doped CZ silicon single crystals, the conversion efficiency distribution has a peak in the range of 5 Ω cm to 0.1 Ω cm as shown in Figure 4 of the present application. This defines a narrower range of resistivities than had been known in the art. My research revealed that a resistivity of more than 5 Ω cm is unnecessarily high, and the conversion efficiency may be reduced

due to internal resistance. In addition, if the resisivity is less than 0.1 Ω cm, the lifetime of the minority carrier will decrease due to Auger recombination, and the conversion efficiency will decrease. Thus, I found that a critical range of resistivities for a gallium-doped CZ silicon single crystal wafer is from 5 Ω cm to 0.1 Ω cm, and that crystals in this range have high conversion efficiencies and can have no photo-degradation.

9. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: April 28, 2003 Takao Abe

Takao Abe

Advanced
Program

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Sept. 20-24/1999

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Light Degradation and Control of Low-Resistivity CZ-Si Solar Cells
— An International Joint Research —

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ABSTRACT

An international joint research has been conducted to investigate light degradation of low-resistivity Si CZ wafers and also to provide how to suppress the degradation. Ten kinds of CZ, MCZ and FZ Si wafers were evaluated under AM1.5 irradiation and processed to fabricate solar cells using low and high temperature processes. Lifetime degradation was suppressed using MCZ Si wafers with low-oxygen content and Ga-doped CZ wafers. In particular, high-temperatue oxidation was also effective to obtain almost no light degradation. No degradation of solar cells could be realized by using B-doped MCZ and Ga-doped CZ wafers combined with a high temperature processing.

1. Introduction

Recently, photovoltaic market has greatly expanded to more than 150 MWp primarily due to an increased production of bulk-type crystalline silicon (c-Si) solar cells [1]. The bulk-type c-Si solar cells are considered to continue to play a major role in near and mid-term PV markets because of the reliable, abundant and non-pollution material nature [2]. Future cost reduction is expected to realize highly efficient (20%) c-Si solar cells with a thinner substrate (<200 μm) structure. As for single crystalline substrates, CZ wafers have been utilized due to the low-cost and high-quality. However, low-resistivity, B-doped CZ-Si wafers with a possibly highest efficiency have an issue of light degradation of cell performance.

Light degradation of B-doped wafers was firstly observed in 1973 [3]. Recent research in 1990's was directed to clarify fundamental understanding of the light degradation [4,5]. The light degradation was ascribed to boron-oxygen pairs created under illumination [6]. To understand the light degradation in more detail and to find a solution to suppress the degradation, international joint research has been conducted on a non-government, private basis. Several kinds of Si wafers were supplied by Shin-Etsu Handotai Co. (SEH) to major international institutions including Sharp Corp., Hitachi, Ltd., Fraunhofer Institute for Solar Energy Systems (FhG-ISE), University of New South Wales (UNSW), Georgia Institute of Technology (GA Tech) and Tokyo University of Agriculture and Technology (TUAT). This paper describes primary results of the joint research on light degradation of low-resistivity CZ wafers and cells, and also suppression of light degradation using CZ wafers with low oxygen content and Ga-doped CZ wafers.

2. PV Market Status and Issue

In the last ten years, the market growth has been remarkableas shown in Fig.1. Especially last year, a world-wide PV market expanded to 150 MWp, 22% increase as compared to 1997. The market size is about 5 times larger than that in 1988. The increase depends upon a great expansion of cell production capacity using single and multicrystalline Si wafers. As for film-type solar cells, the cell production had been almost constant except for a substantial increase of the a-Si solar cells. As a whole, bulk-type crystalline silicon solar cells are still dominated in the current photovoltaic market for both remote and grid-connected power applications.

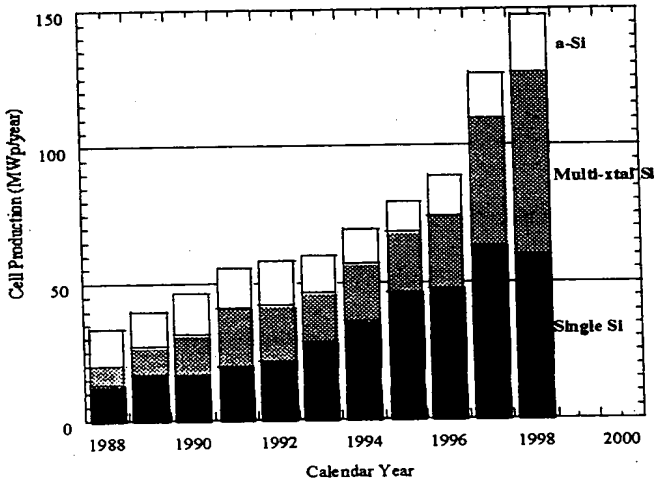

Fig. 1 Yearly cell production of single-Si, multicrystalline Si and a-Si solar cells.

Cost reduction of solar modules is a key factor for future cost reduction of the PV systems. Government module price in Japan, so-called NEDO price, is saturated to be about 600 yen (4.3$)/Wp [7]. It was pointed out there is a big cost gap between the current market price and the government cost forcast of 200 yen/Wp. The module cost consists of three factors including Si materials, cells and modules. Although a major part is the Si materials, all the factors should be reduced to at least one third of the current price. The cost of cell production was expected to reduce drastically by an automated mass-production, whereas new ideas are required for the cost reduction of Si materials and modules.

To solve the cost gap between the current price and government cost analysis, Japanese government has just decided to promote a new four-year R&D program for multicrystalline silicon solar cells. Primary targets are to achieve a very high cell efficiency of 20% and lower production cost of 147 yen/Wp. The cost reduction would be realized using a very thin substrate of 150 μm.

3. Light Degradation of CZ Wafers and Cells

Experimental

(a) Si wafer specification

Ten kinds of Si wafers supplied by Shin-Etsu Handotai Co. (SEH) consisted of conventional CZ, MCZ(magnetic-field applied CZ) and FZ crystals with Boron or Gallium impurity with various oxygen concentrations. Table 1 shows measured results of resistivity and oxygen content reported by TUAT. MCZ technology was effective to reduce the oxygen content in the Si crystals which comes from preventing convection in Si melt during CZ growth.

Table 1 Specifications and light degradation of carrier lifetimes for CZ, MCZ and FZ wafers. (TUAT)

Sample No.	Growth method and dopant	Resistivity (Ωcm)	Oxygen content (ppma)	Lifetime(μm)	
				Initial	After (rel.)*
1	CZ, B-doped	0.64	8.21	57	6.08 (0.11)
2	CZ, B-doped	0.69	14.5	38	3.56 (0.09)
3	MCZ, B-doped	4.80	11.9	286	137 (0.48)
4	MCZ, B-doped	1.07	3.28	247	104 (0.42)
5	MCZ, B-doped	4.33	2.93	1165	727 (0.62)
6	FZ, B-doped	0.63	<0.1	33	100 (3.0)
7	FZ, B-doped	3.98	<0.1	128	159 (1.23)
8	CZ, Ga-doped	2.49	9.45	567	398 (0.70)
9	CZ, Ga-doped	4.12	10.5	827	302 (0.37)
10	CZ, Ga-doped	24.5	9.61	2380	751 (0.32)

*: Lifetime values after AM1.5 irradiation for 1440 min.

(b) Evaluation of light-irradiated Si wafers

Before lifetime measurement, the Si wafers were annealed at 350C for 30 min to restore minority-carrier lifetimes to a high level status [3]. At TUAT, the surfaces of the light-irradiated wafers were passivated chemically using an iodine-ethanol solution. The Si wafers were irradiated under AM1.5 simulated sunlight until 24 hours. After dipping in HF solution to remove native oxide, the Si wafers were immersed in a 3 percent of iodine ethanol solution. Lifetime measurement was carried out using μ-wave reflection photoconductivity decay without bias light. The measurement was conducted at 13 different points on a 4-inch wafer and then averaged. At FhG-ISE, the Si surfaces were oxidized at 1050C and annealed in forming gas at 425C. Then, effective lifetimes were measured under a bias light of 0.5 suns after applying corona charges. This treatment was effective to obtain bulk lifetimes.

(c) Fabrication and evaluation of Si solar cells

Solar cells were fabricated at the several institutes using different technologies. FhG-ISE and UNSW used high-efficiency cell fabrication processes, so-called the RP-PERL and PERL processes. The feature of the RP-PERL process is the local back-surface-field (BSF) under the local rear contact [8].

PERL processes. The feature of the RP-PERL process is the local back-surface-field (BSF) under the local rear contact [8].
The solar cells were irradiated and measured under AM 1.5 simulated sunlight at appropriate times. A simple belt-line cell fabrication process at Sharp Corp. includes texture etching, $POCl_3$ diffusion, SiO_2 passivation at 800C, TiO_2 AR coating, screened Al-BSF and printed Ag electrodes. A similar belt-line process was used at GA Tech consisting of belt-line furnace diffusion, SiNx AR coating and screen-printed Ag electrodes.

Results and Discussion

(a) Variation of carrier lifetimes for as-received and oxidized Si wafers under AM1.5 irradiation

Firstly, carrier lifetimes of as-received Si wafers were measured before and after AM1.5 irradiation. As shown in Fig.2, carrier lifetimes tended to decrease exponentially with time under irradiation except for FZ crystals of #7. The lifetimes of the FZ wafers were found to increase slightly with time. Further research is needed to understand the behavior. On the other hand, the lifetimes of conventional low-resistivity CZ wafers of #1 and 2 decreased with irradiation time to about one tenth of initial values before irradiation. However, in the use of B-doped MCZ and Ga-doped CZ, light degradation of carrier lifetimes was suppressed substantially. Especially, the MCZ wafers of #4 and 5 showed less light degradation due to the low oxygen content. The Ga-doped wafers of # 8 to 10 were also effective to suppress light degradation even if oxygen content was as high as 10 ppma.

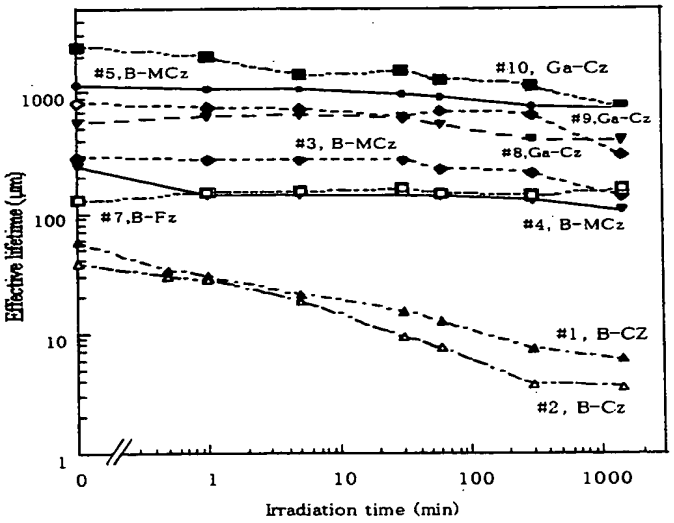

Fig. 2 Variation of effective lifetimes for as-received Si wafers under AM 1.5 illumination. (TUAT)

As for oxidized Si wafers conducted at FhG-ISE, a different behavior was obtained for the lifetime variation after light irradiation. As indicated as a dotted curve in Fig.3, variation ratios of lifetimes for the as-received and oxidized CZ wafers of #1 and 2 were almost the same, whereas ratios for other B-doped MCZ, FZ and Ga-doped CZ wafers were close to one, indicating no degradation. The latter behavior was different from that for the as-received wafers. The difference is probably due to the fact that defect concentration can be reduced significantly

by high temperature processes such as oxidation [5].

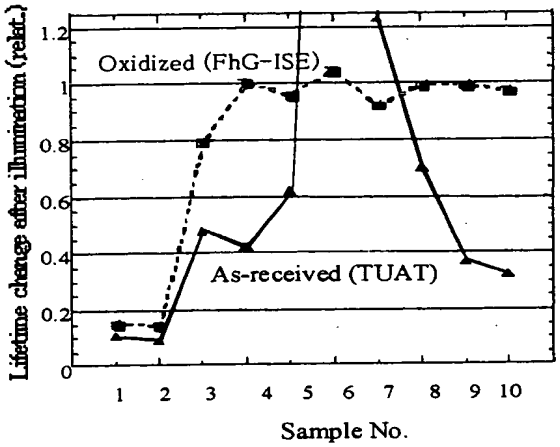

Fig. 3 Comparison of lifetime variation under AM 1.5 irradiation for as-received and oxidized Si wafers carried out at TUAT and FhG-ISE, respectively.

(b) Degradation and suppression of cell performance under AM 1.5 irradiation

Light degradation of cells fabricated using a low temperature process at Sharp was investigated. The cell efficiencies did not vary greatly although the lifetimes varied drastically as indicated in Table 1. The difference between wafers and cells might be a small effect of lifetime on conversion efficiency in a high lifetime region. As shown in Fig. 4, conversion efficiencies of CZ cells of #1 and 2 decreased after irradiation, whereas light degradation disappeared for higher-resistivity cells. MCZ cells of #3, 4 and 5 were stable under the irradiation although the carrier lifetimes decreased as shown in Fig. 3. This is considered by changing the crystal quality at the oxidation temperature of 800 C. As for the effect of oxygen content, the light degradation tended to increase with oxygen content as shown in Fig. 5. Light degradation was suppressed by reducing the oxygen content to 3.3 ppma as shown in the MCZ cells. The low oxygen content was realized by a quasi-static growth condition of magnetic-applied CZ pulling (MCZ). No light degradation was observed for FZ cells of #6 and 7 irrespective of various oxygen content and resistivity.

A Ga-doped cell of #8 with a relatively high oxygen content of around 10 ppma was effective to suppress light degradation as shown in Fig. 6. Efficiencies of other two Ga-doped cells of # 9 and 10, as shown in Fig. 4, decreased slightly at an irradiation time of 2 hr. This tendency is similar to that for lifetime decrease under irradiation shown in Fig. 3 except for the MCZ cells. The quality of the MCZ crystals might change at the oxidation temperature of 800 C.

However, the Sharp cell results in Fig. 4 are a little different from cell data obtained at FhG-ISE where a high oxidation temperature of 1050C was utilized. As shown in Fig. 7, no degradation was obtained for MCZ cells of #4 and 5, FZ cells of #6 and 7 and Ga-doped CZ cells of # 8, 9 and 10. These cell results are consistent with the lifetime data shown in Fig. 3. The difference between the low and high temperature processes might cause the change of crystal quality. Further research would be required, i.e. the change of interstitial oxygen into substitutional sites, formation of inactive SiO_2 precipitates, interaction between B or Ga atoms with interstitial oxygen atoms, etc.

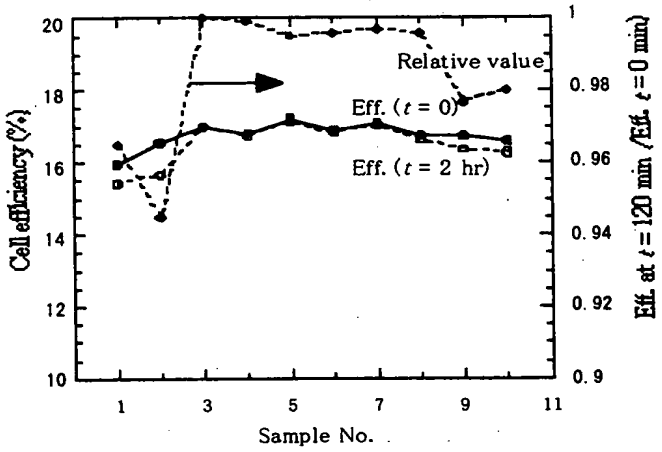

Fig. 4 Conversion efficiencies of Sharp cells fabricated by a low-temperature process before and after AM 1.5 irradiation.

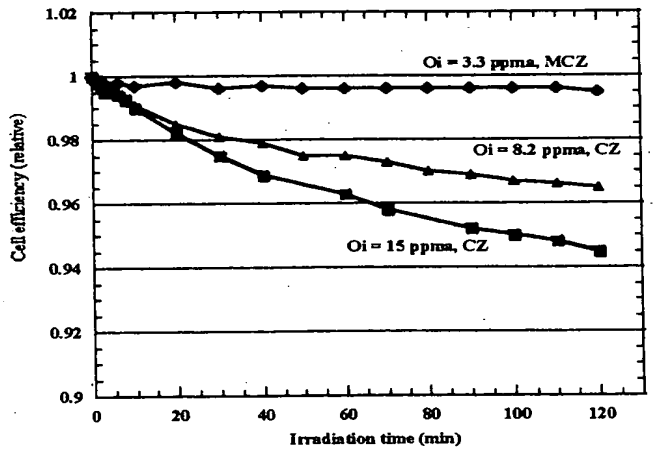

Fig. 5 Effect of oxygen content in CZ crystals on light degradation of carrier lifetimes. (Sharp cells).

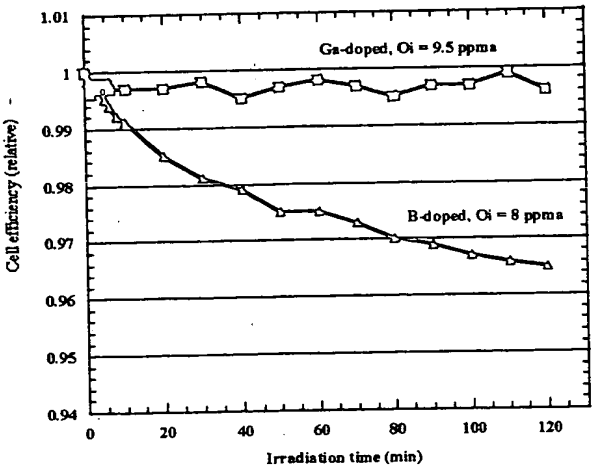

Fig. 6 Effect of impurity species in CZ crystals on light degradation of carrier lifetimes. (Sharp cells).

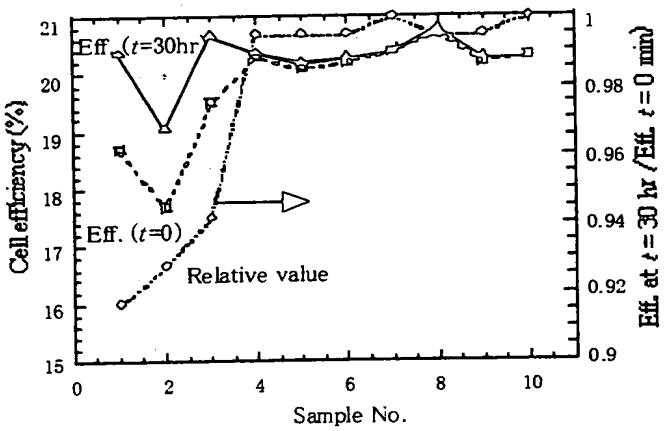

Fig. 7 Conversion efficiencies of FhG-ISE cells fabricated by a high-temperature process before and after AM 1.5 irradiation.

4. Conclusion

Primary results throughout the international joint work are described below.

(1) Light degradation occurred for low-resistivity B-doped CZ wafers with a high oxygen content suggesting the existence of a boron-oxygen complex for the light degradation.

(2) Almost no light degradation was found for Si solar cells using MCZ and FZ single wafers including interstitial oxygen content less than a few ppma.

(3) Ga-doped CZ cells showed no or small light degradation even if the wafers contain high oxygen content.

(4) A high-temperature oxidation was effective to obtain no light degradation of Si cells fabricated using B-doped MCZ and Ga-doped wafers.

(5) Highly efficient solar cells with cell efficiencies as high as 20% were fabricated using the low resistivity MCZ and Ga-doped CZ wafers.

From these results, it is concluded that MCZ and Ga-doped CZ wafers are the promising materials for future advancement toward highly efficient and low-cost solar cells.

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SPECIAL PAPER AWARD

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